Supporting Information

Unusual Formation of Thiaisoporphyrins from 21-Thiaporphyrins†

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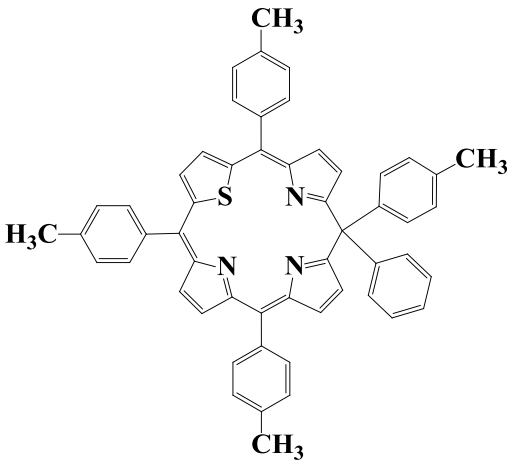

Compound 2
Mol. Wt. = 763.98
Peak at $[M+2H]^+$ = 766.3265

Indian Institute of Technology (B)

Analysis Info

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Method	Tune_pos_Standard_NAI-1000.m	Operator	IIT-B
Sample Name	MR-AG-TN3S	Instrument	maXis impact 282001.00081
Comment	C54H44N3S		

Acquisition Parameter

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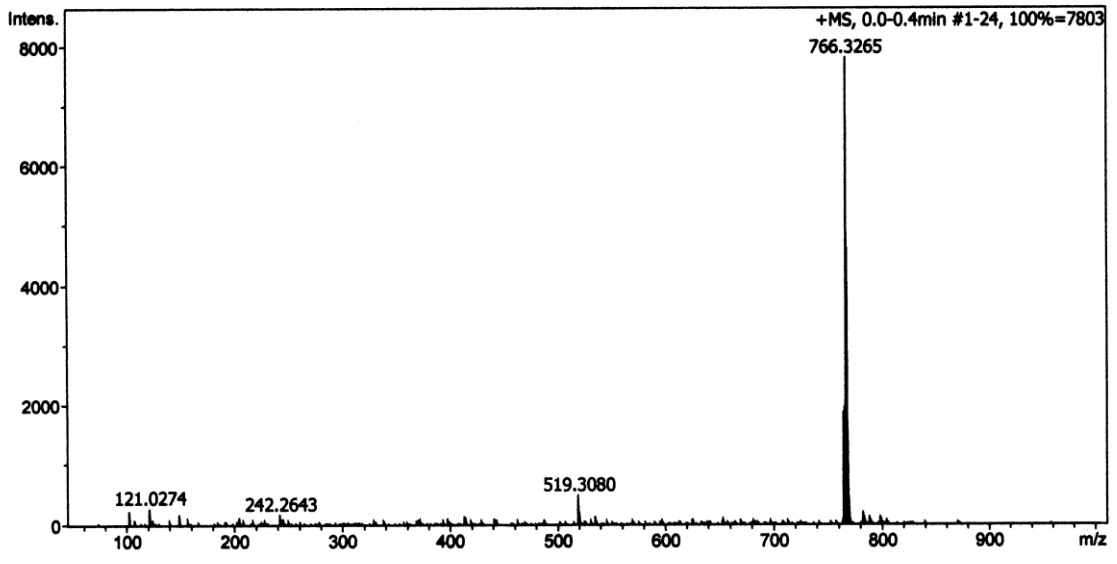
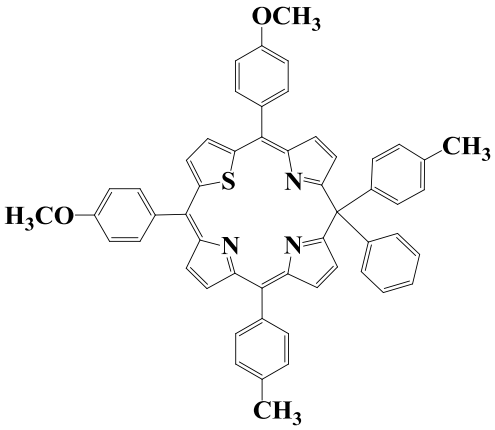
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	400.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
766.3265	1	C54H44N3S	766.3250	1.8	12.3	1	100.00	34.5	even	ok

Figure S1. HR–MS spectrum of compound **2**.

S3



Compound 3
Mol. Wt. = 795.98
Peak at $[M]^+$ = 796.3003

Indian Institute of Technology (B)

Analysis Info

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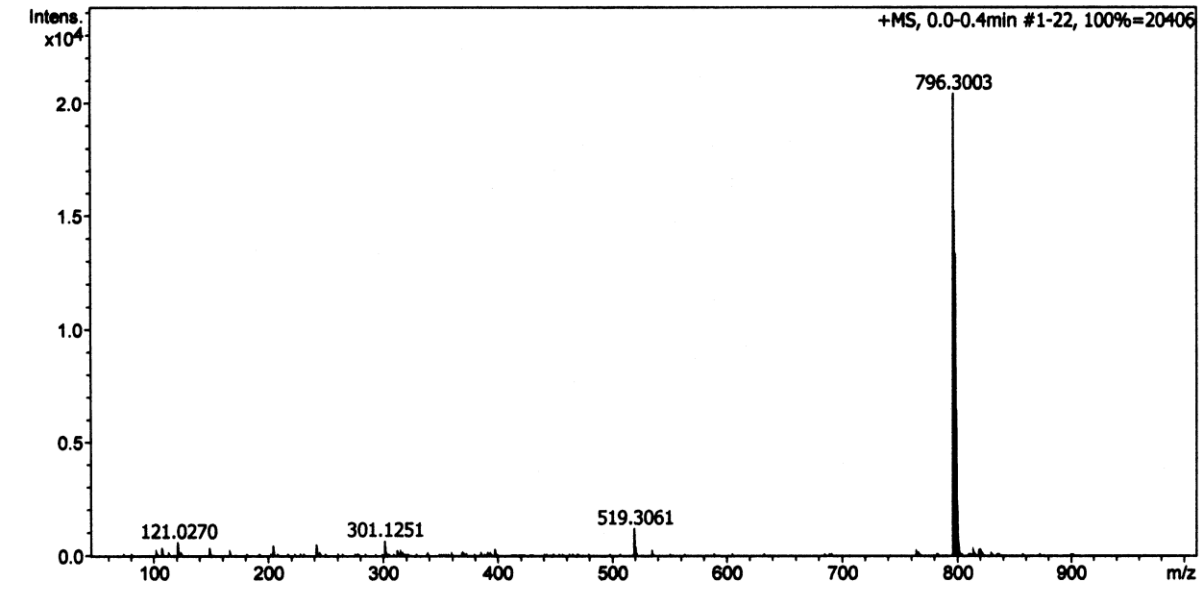
Method	Tune_pos_Standard_NAI-1000.m	Operator	IIT-B
Sample Name	MR-AG-DTN3S	Instrument	maXis impact 282001.00081
Comment	C54H41N3O2S		

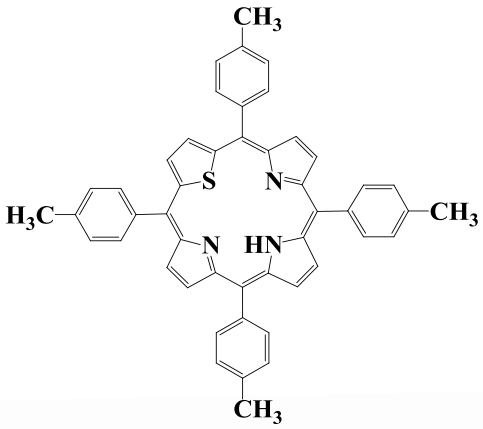
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.1 Bar
Focus	Active	Set Capillary	3500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	400.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
796.3003	1	C54H42N3O2S	796.2992	-1.4	231.6	1	100.00	35.5	even	ok

Figure S2. HR–MS spectrum of compound **3**.



Compound 4

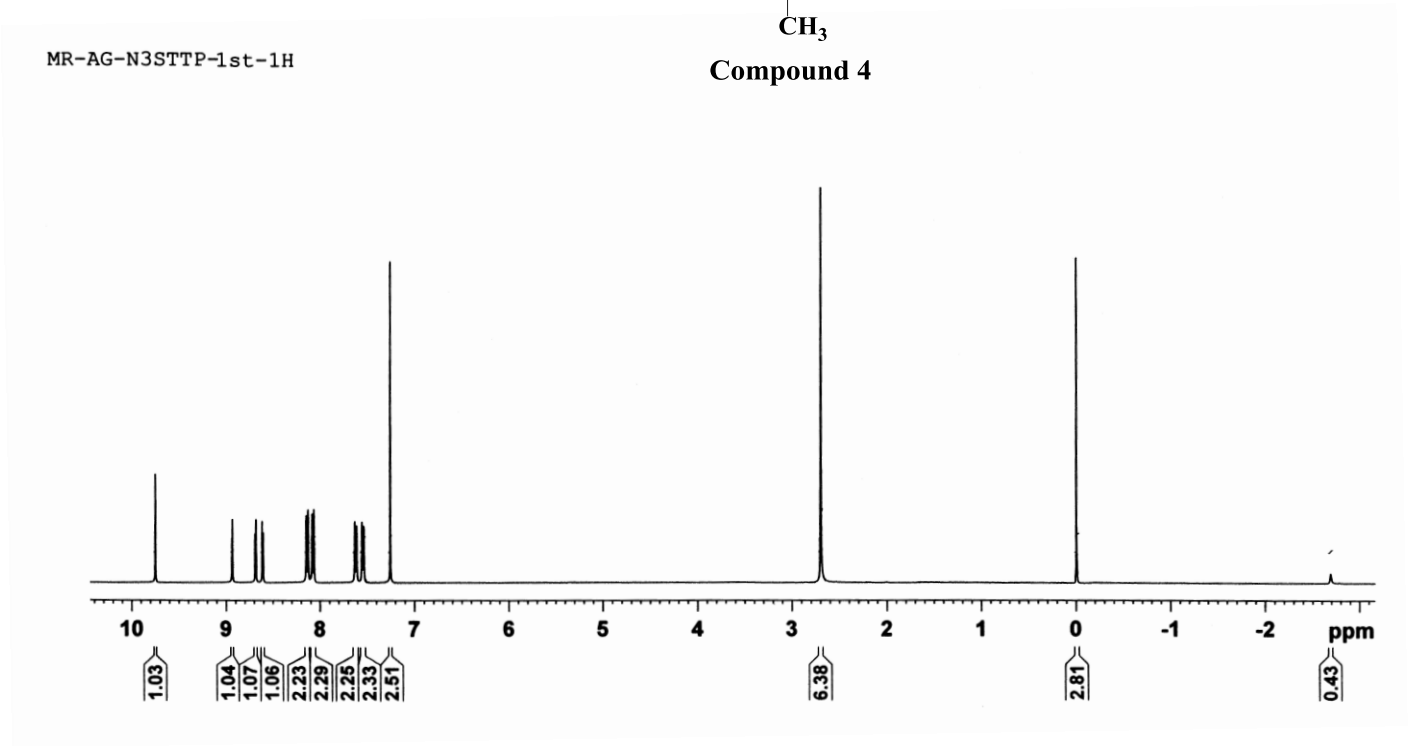


Figure S3. ^{1}H NMR spectrum of compound **4** recorded in $CDCl_3$ at room temperature.

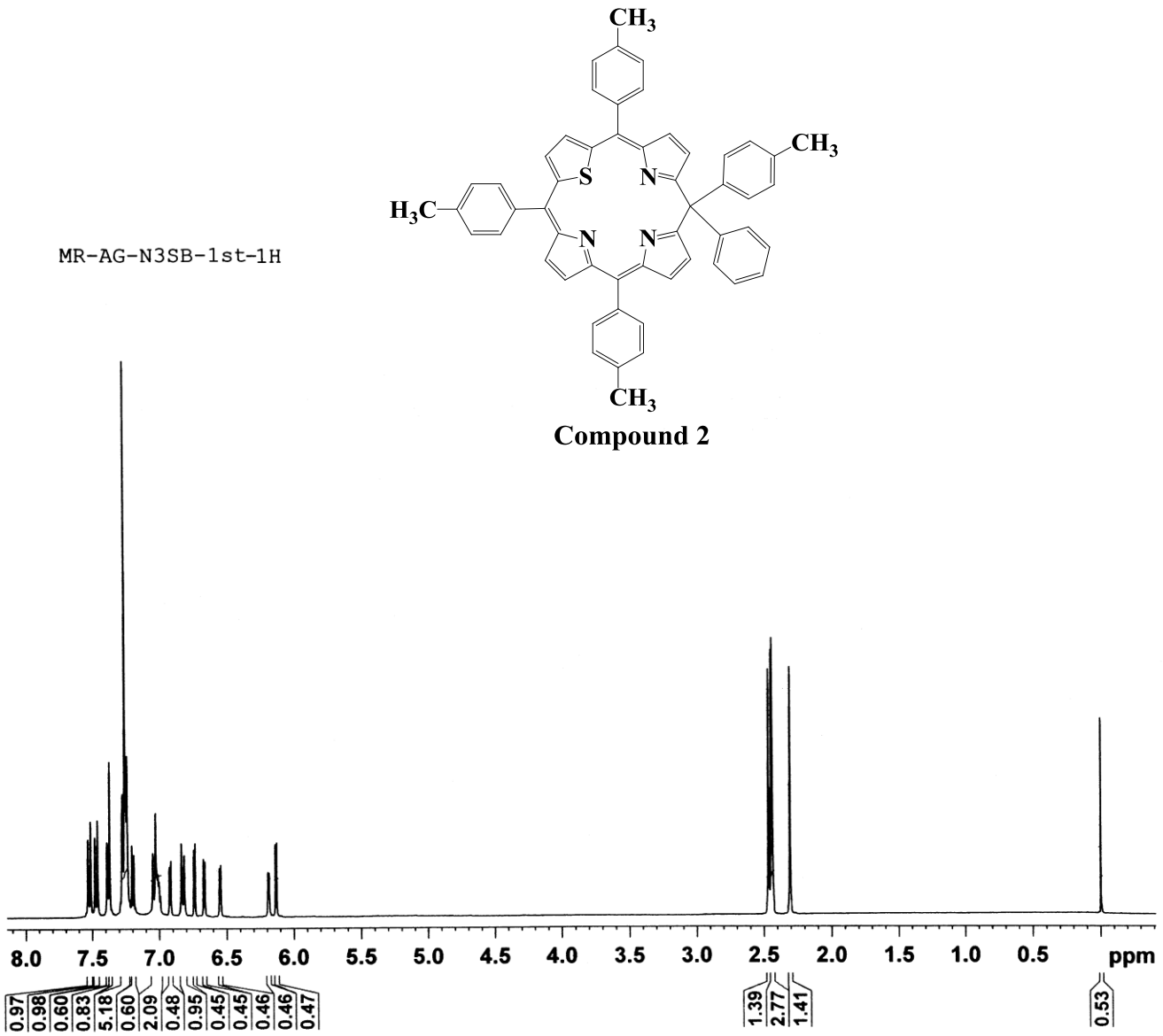
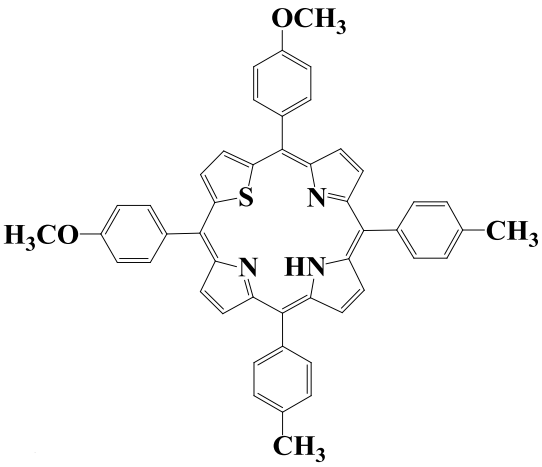


Figure S4. ^{1}H NMR spectrum of compound **2** recorded in $CDCl_3$ at room temperature.



MRK-AG-N3SDTDM-1H

Compound 5

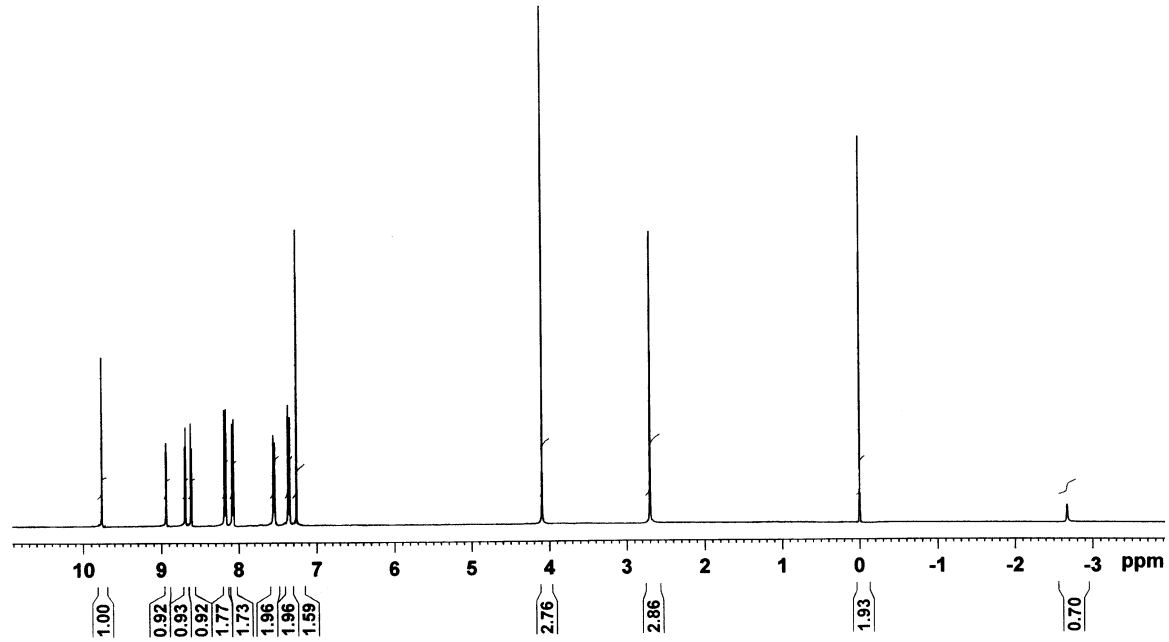
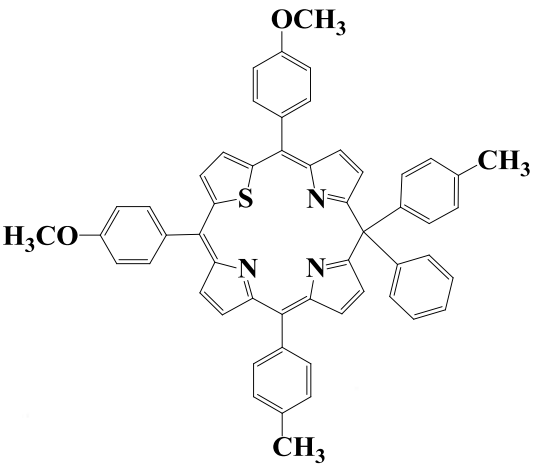


Figure S5. ^{1}H NMR spectrum of compound **5** recorded in $CDCl_3$ at room temperature.



MR-AG-BN3SDTDM-1H

Compound 3

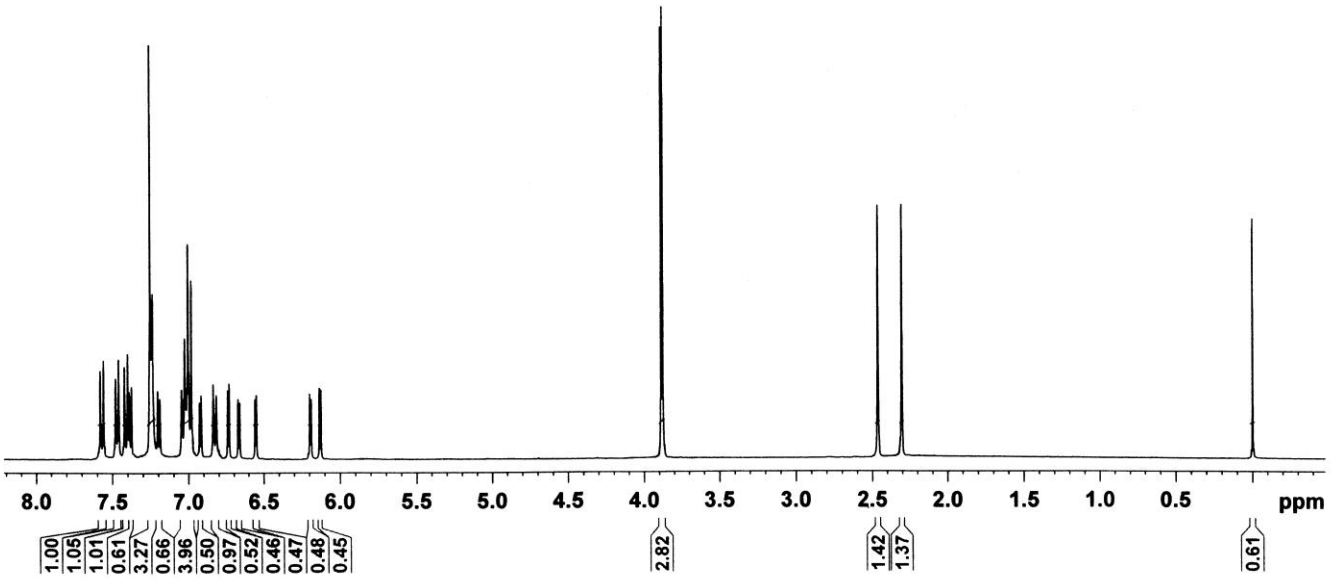


Figure S6. ^{1}H NMR spectrum of compound **3** recorded in $CDCl_3$ at room temperature.

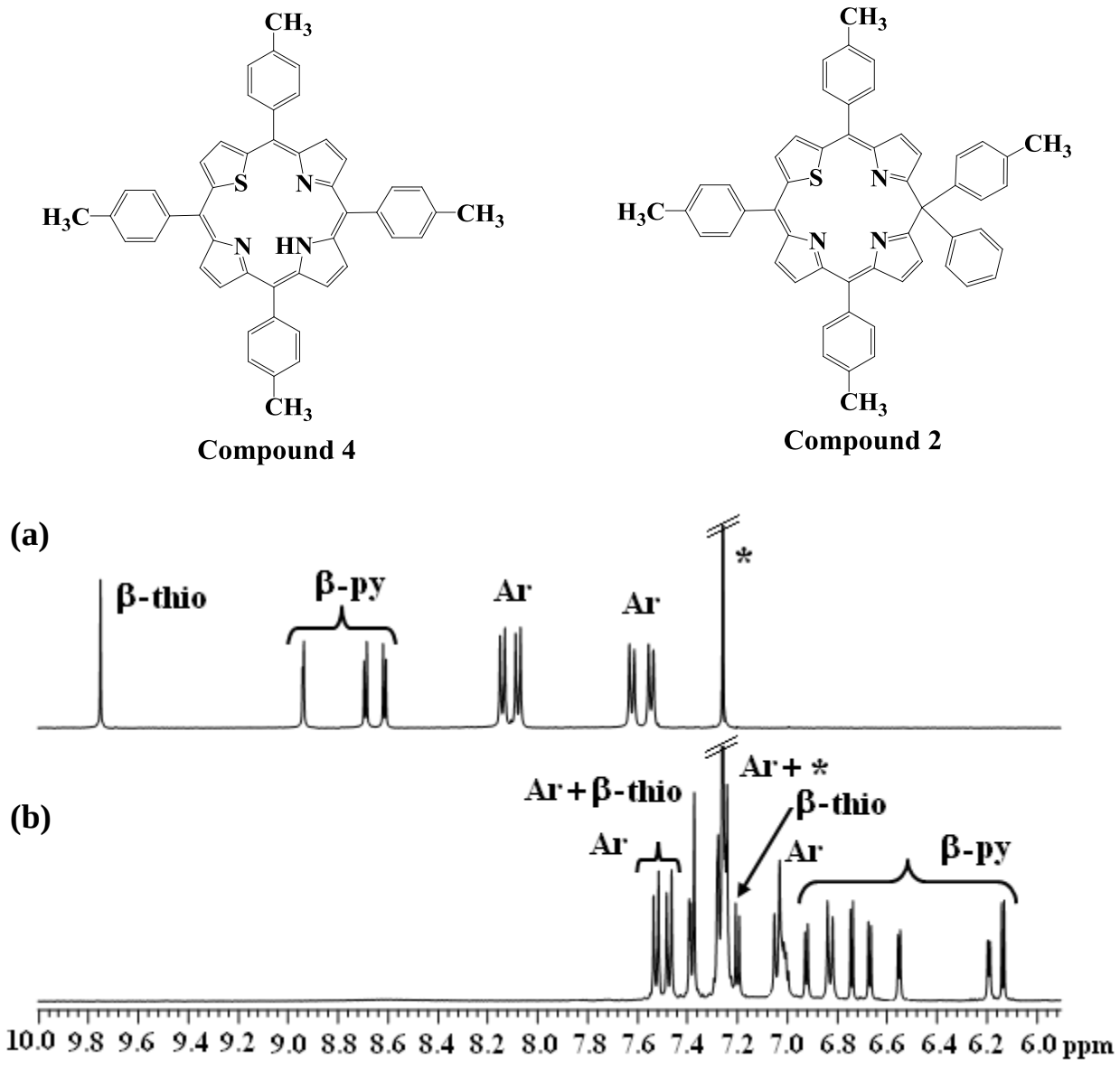
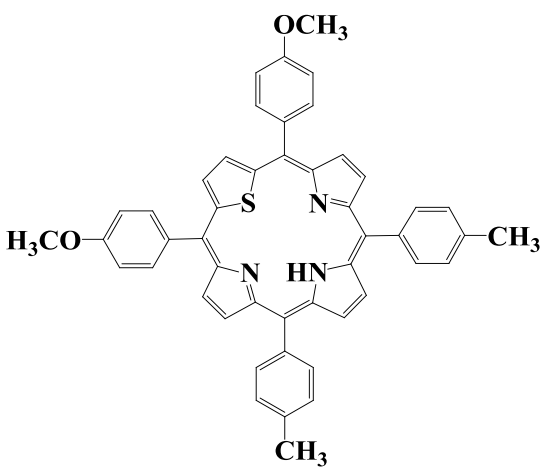
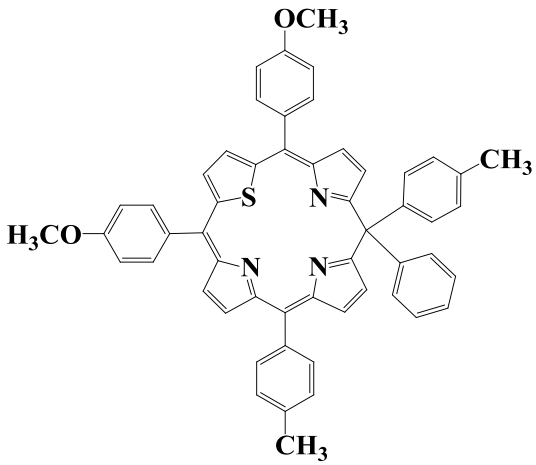


Figure S7. Comparison of ^{1}H NMR spectra of compounds (a) **4** and (b) **2** recorded in $CDCl_3$ at room temperature.



Compound 5



Compound 3

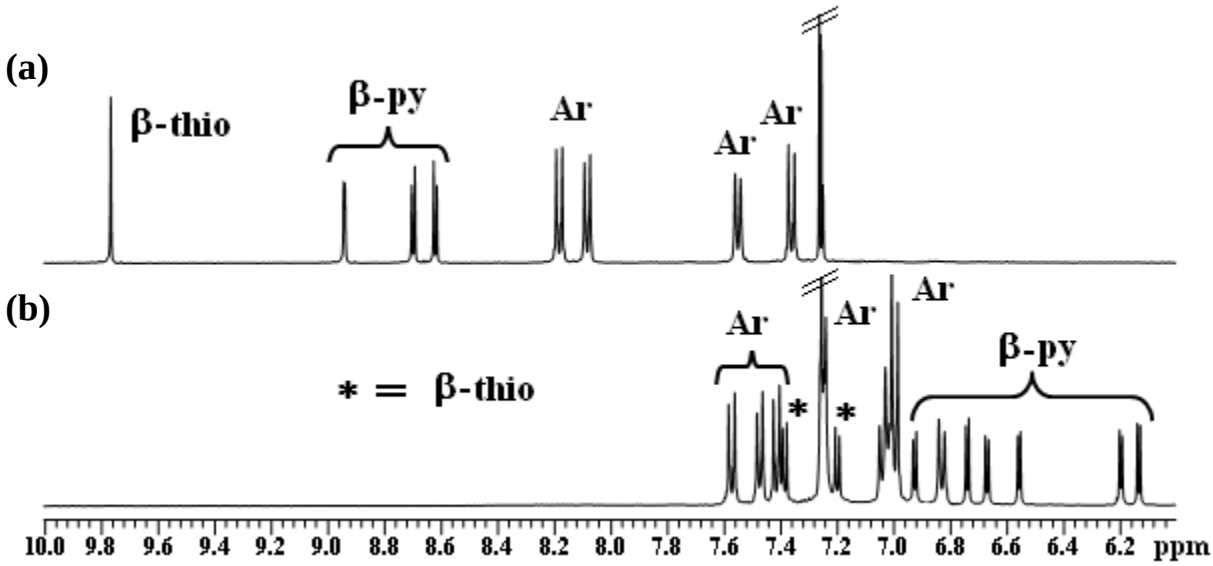


Figure S8. Comparison of ^{1}H NMR spectra of compounds (a) **5** and (b) **3** recorded in $CDCl_3$ at room temperature.

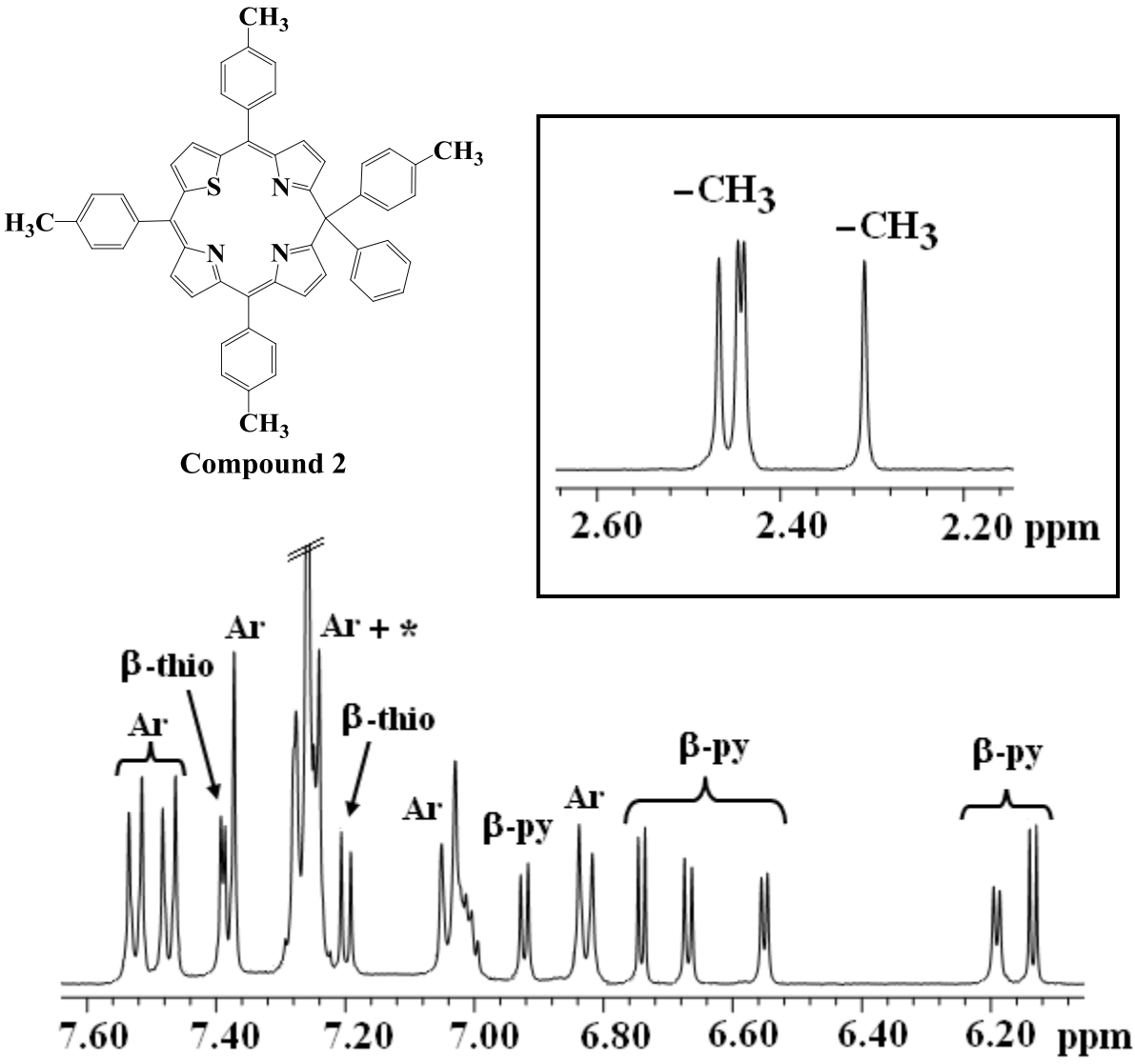
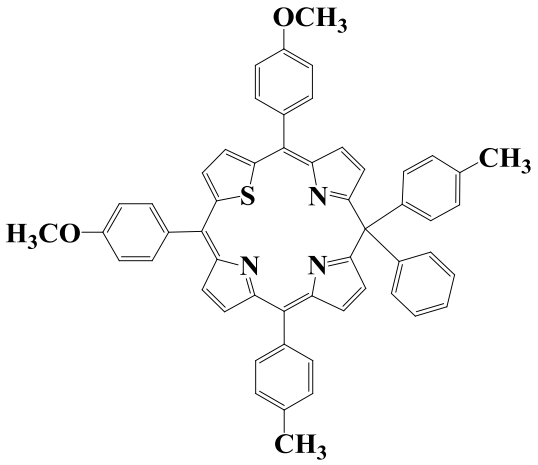


Figure S9. Expanded region of ^{1}H NMR spectra for compound **2** recorded in $CDCl_3$ at room temperature.



Compound 3

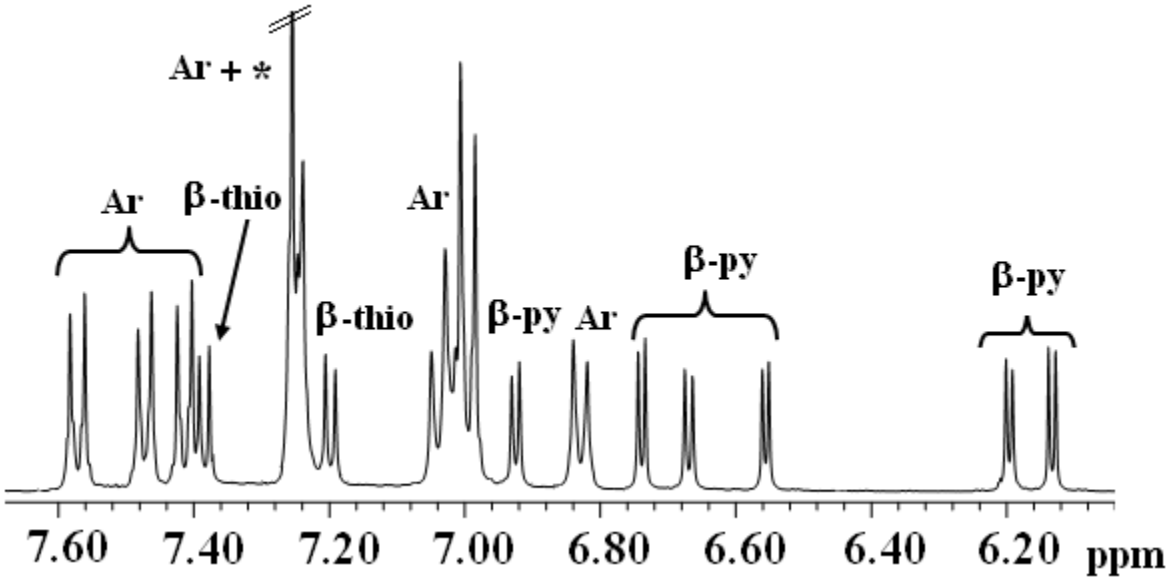
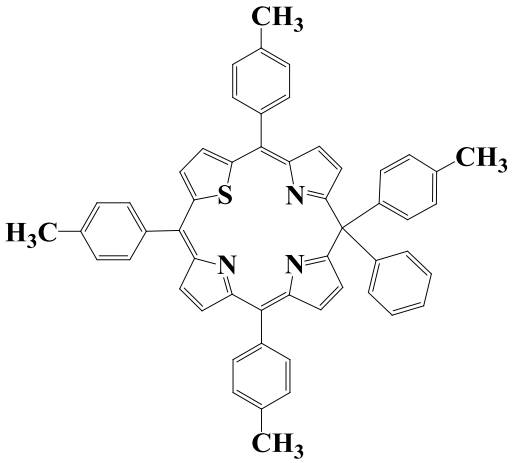


Figure S10. Expanded region of ^{1}H NMR spectra for compound **3** recorded in $CDCl_3$ at room temperature.



Compound 2

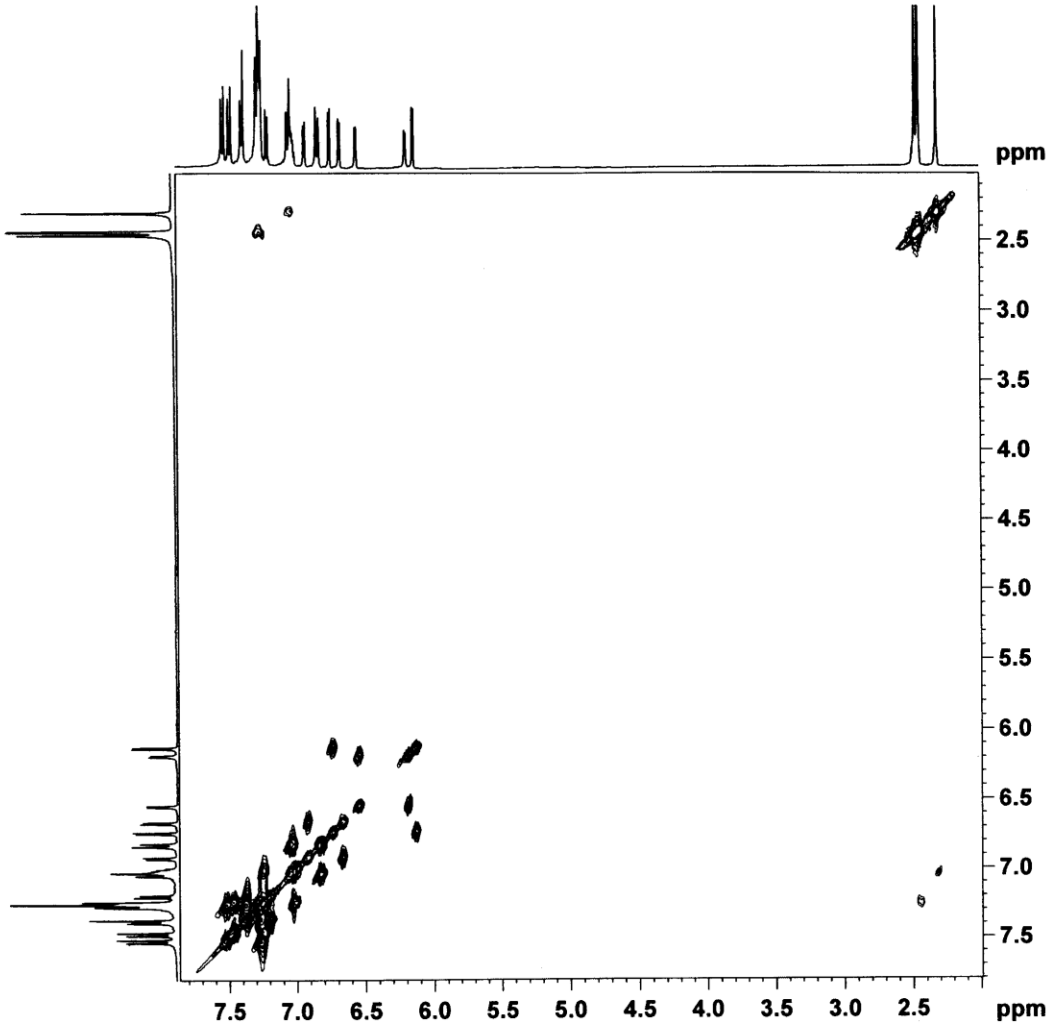
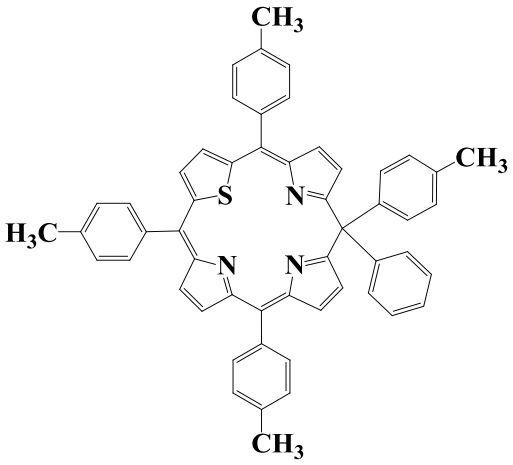


Figure S11. Partial $^{1}H–^{1}H$ COSY spectrum of compound **2** recorded at room temperature in $CDCl_3$.



Compound 2

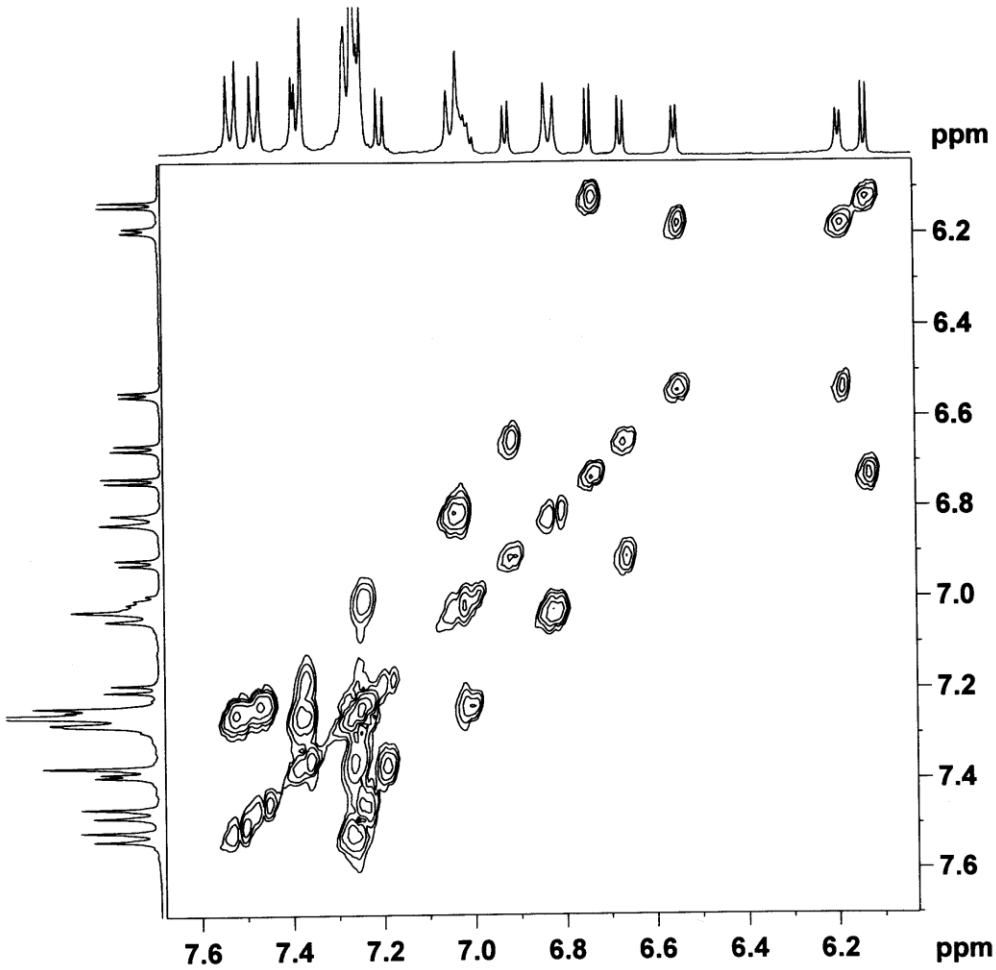
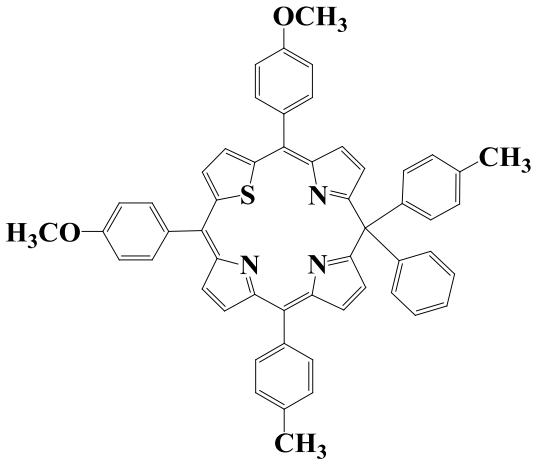


Figure S12. Expanded region of ^{1}H–^{1}H COSY spectrum of compound **2** recorded in $CDCl_3$ at room temperature.



Compound 3

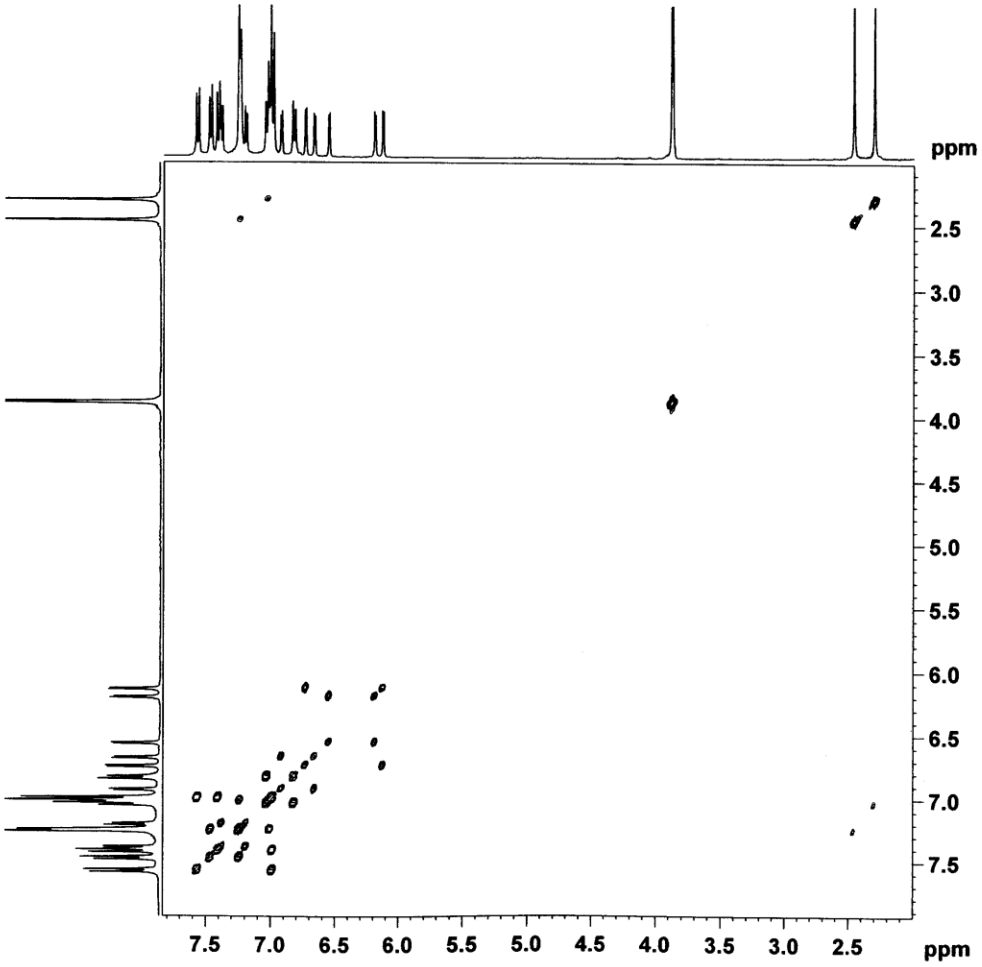
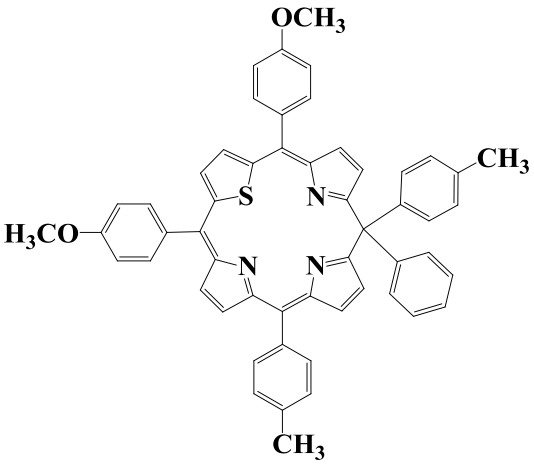


Figure S13. Partial $^{1}H–^{1}H$ COSY spectrum of compound **3** recorded at room temperature in $CDCl_3$



Compound 3

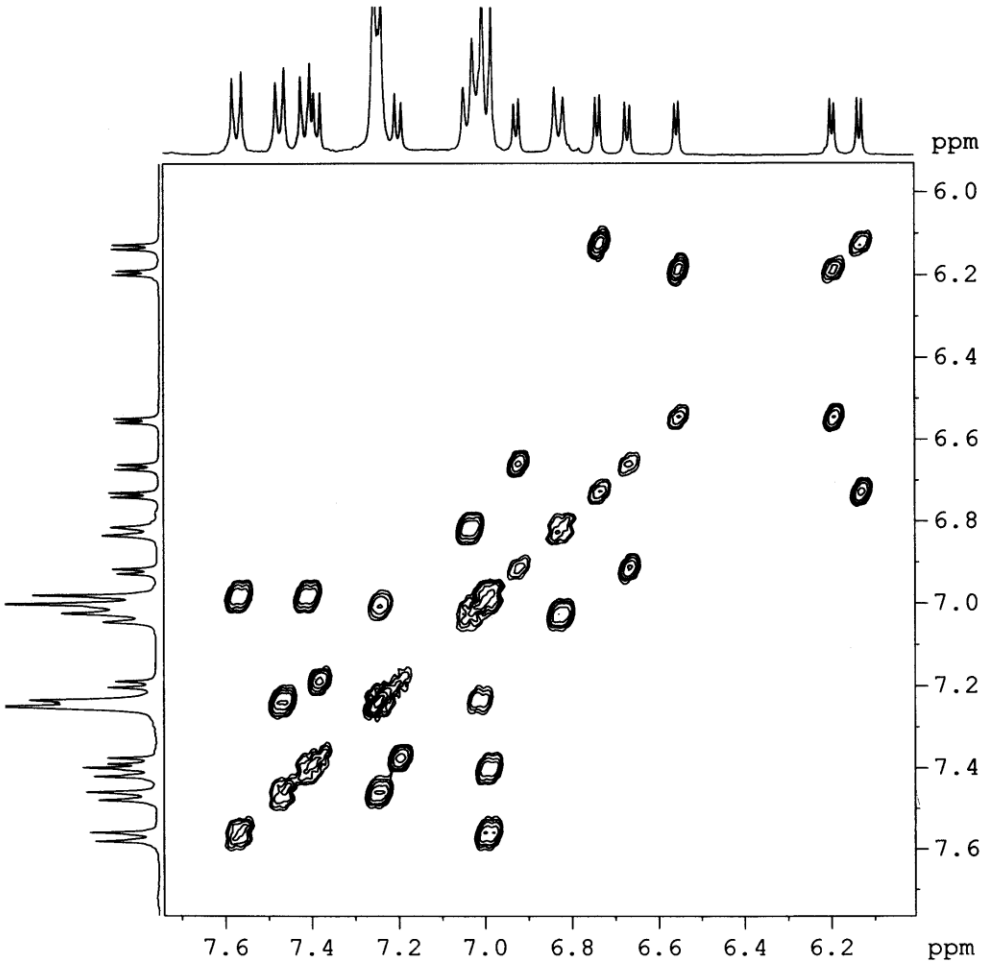


Figure S14. Expanded region of ^{1}H–^{1}H COSY spectrum of compound **3** recorded in $CDCl_3$ at room temperature.

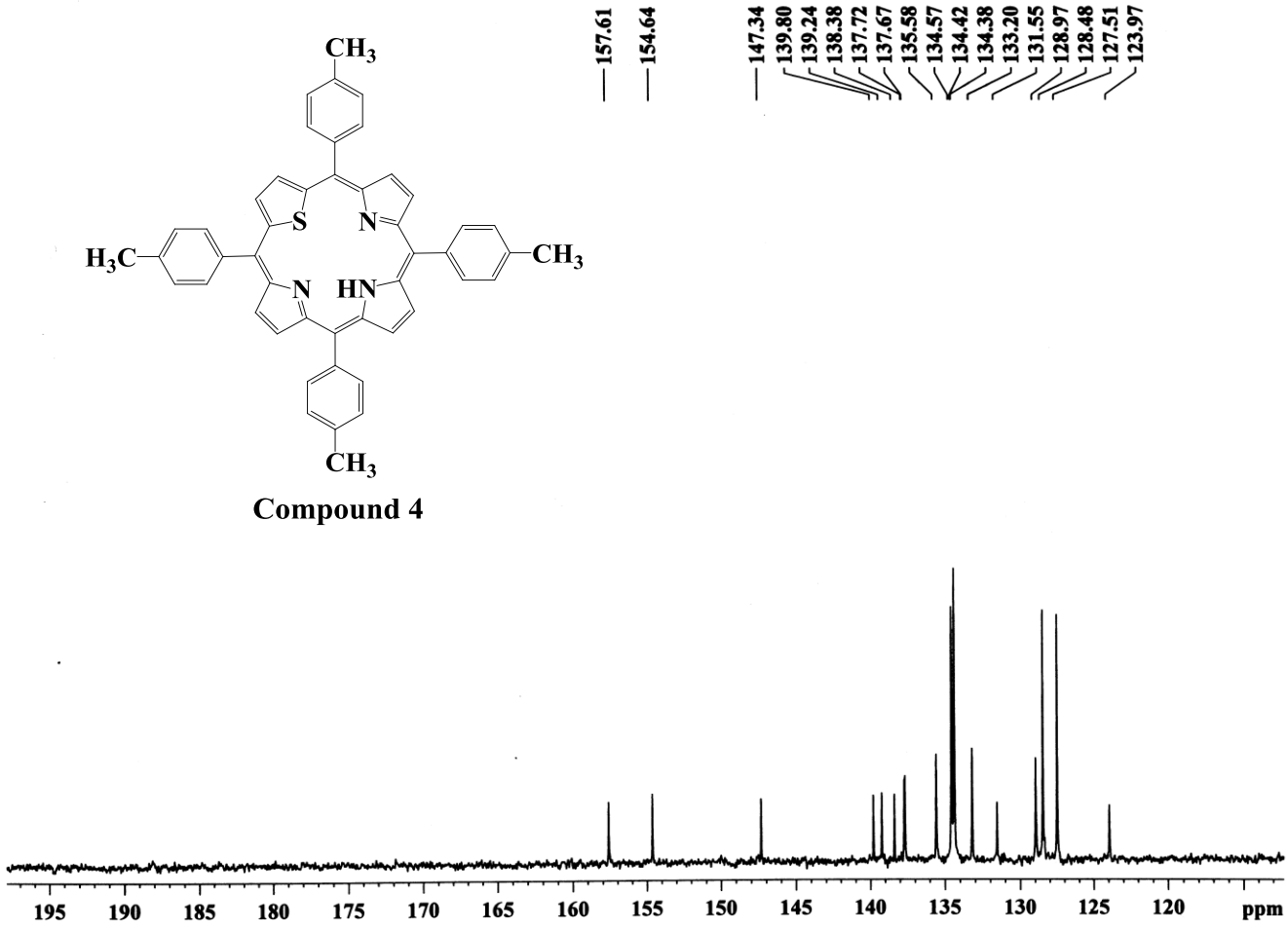
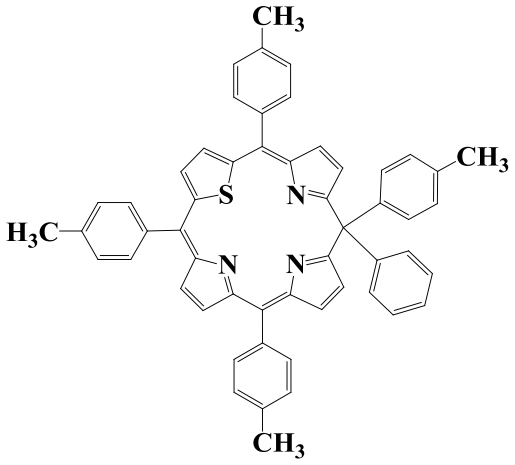


Figure S15. ^{13}C NMR spectrum of compound **4** recorded in $CDCl_3$ at room temperature.



Compound 2

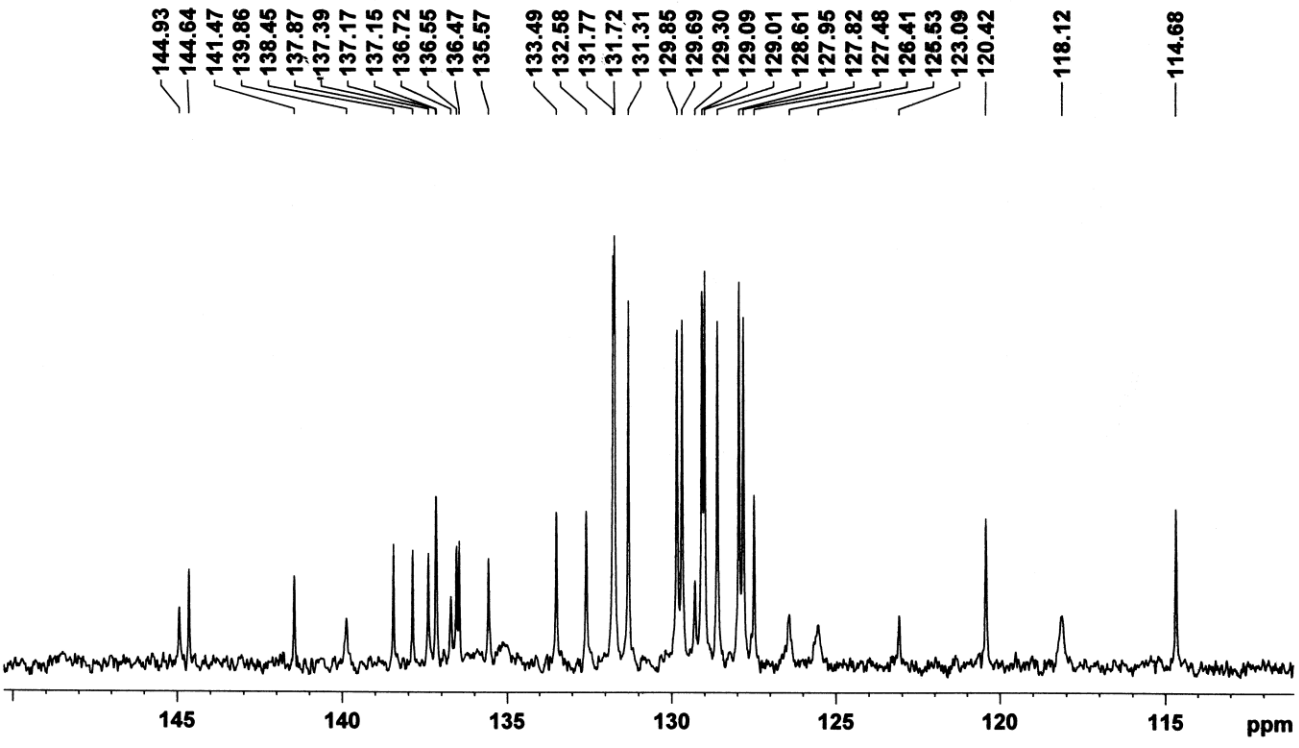
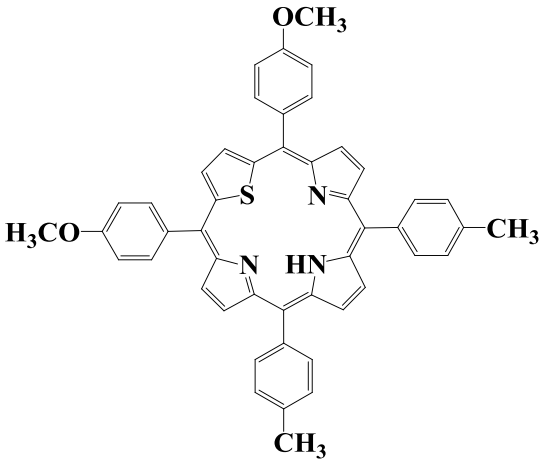


Figure S16. ^{13}C NMR spectrum of compound **2** recorded in $CDCl_3$ at room temperature.



Compound 5

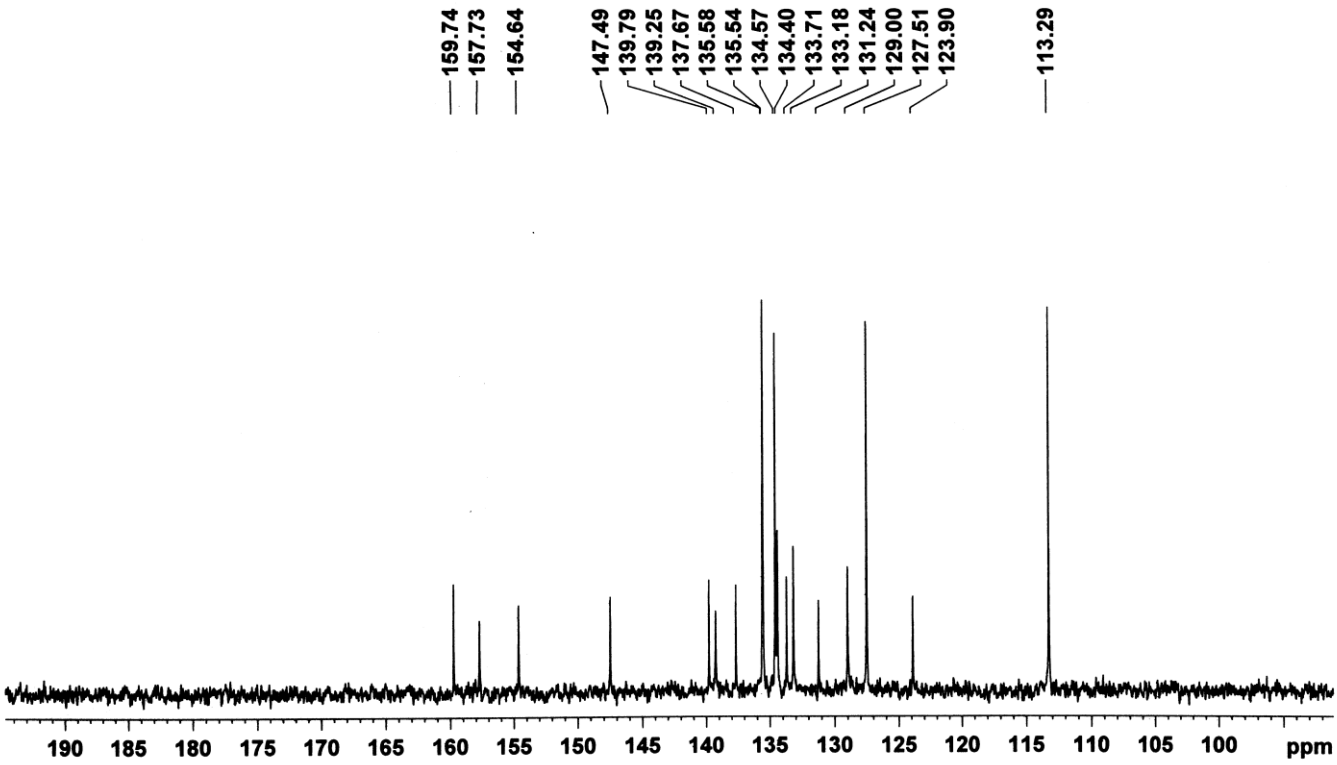
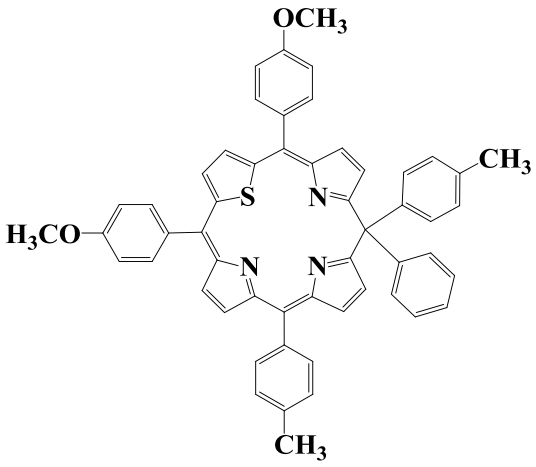


Figure S17. ^{13}C NMR spectrum of compound **5** recorded in $CDCl_3$ at room temperature.



Compound 3

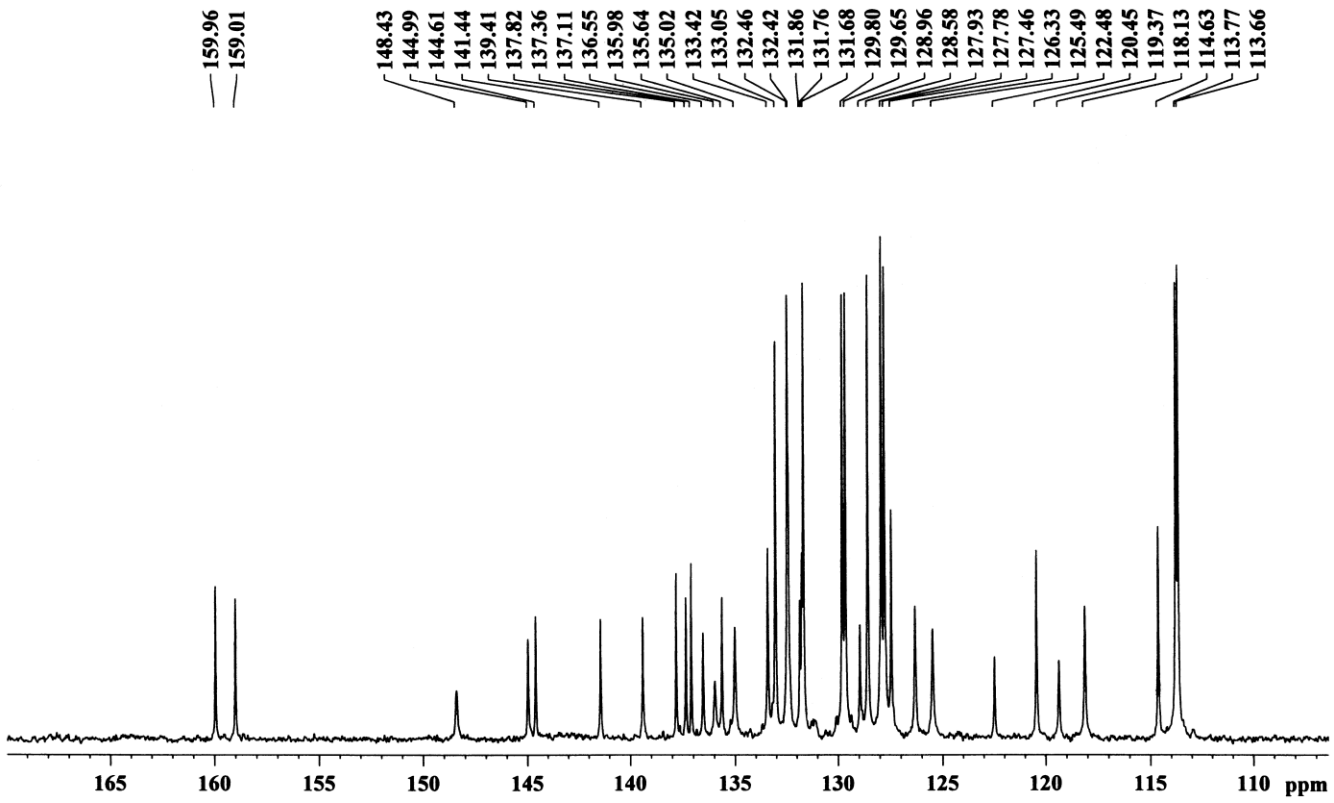


Figure S18. ^{13}C NMR spectrum of compound **3** recorded in $CDCl_3$ at room temperature.

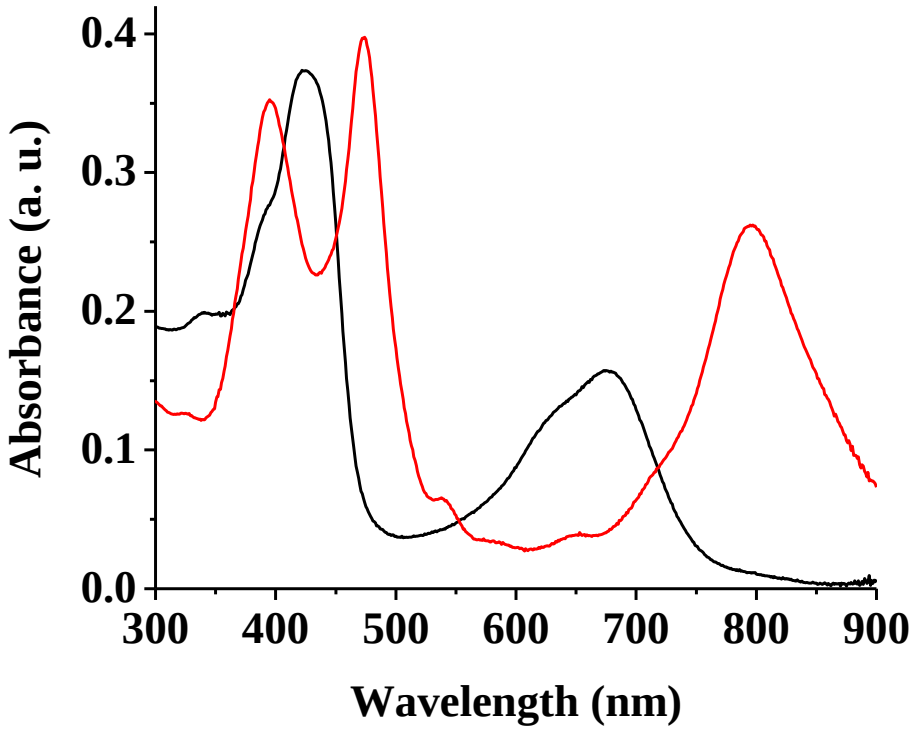


Figure S19. Comparison of absorption spectra of compound **3** (black) and **3+TFA** (red) recorded in CH_2Cl_2 at room temperature. Concentrations used were ~ 10^{-5} M for both the compounds.

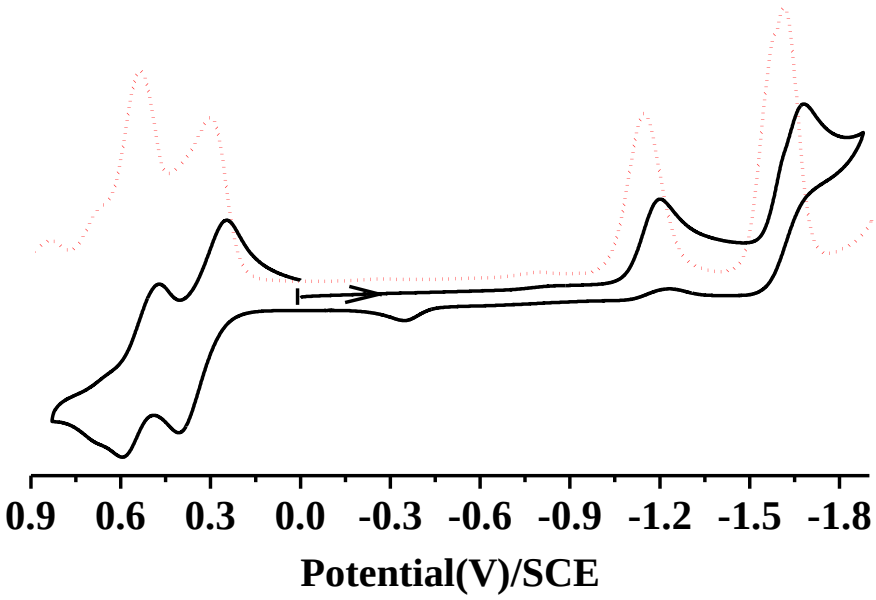


Figure S20. Redox waves of cyclic voltammograms along with differential pulse voltammograms of compound **3** recorded in CH_2Cl_2 solvent using 0.1 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte and saturated calomel electrode (SCE) as reference electrode at scan rates of 50 mVs^{-1}.

Table S1. Absorption and redox data[a].

Compounds	Absorption data Soret band (*log ε*)	Q-bands (*log ε*)	Redox data oxidation (V)	reduction (V)
4	427 (5.42)	483(sh), 513 (4.32), 547 (3.72), 616 (3.44), 676 (3.62)	1.08 1.48	−1.02 −1.35
2	340 (sh), 421 (4.61), 432 (sh)	625 (sh), 672 (4.19, br)	0.61 0.34	−1.14 −1.59
2+TFA	297 (sh), 395 (4.64), 470 (4.67)	539 (sh), 539 (sh), 783 (4.45, br)	–	–
5	431(5.43)	485 (sh), 517 (4.31), 553 (3.73), 619 (3.44), 672 (3.63)	1.06 1.43	−1.01 −1.31
3	339 (sh), 425 (4.57, br)	636 (sh), 675 (4.20, br)	0.55 0.31	−1.13 −1.60
3+TFA	296 (sh), 395 (4.54), 474 (4.60)	537 (sh), 645 (sh), 795 (4.42, br)	–	–

[a] data were collected in CH_2Cl_2 at room temperature.

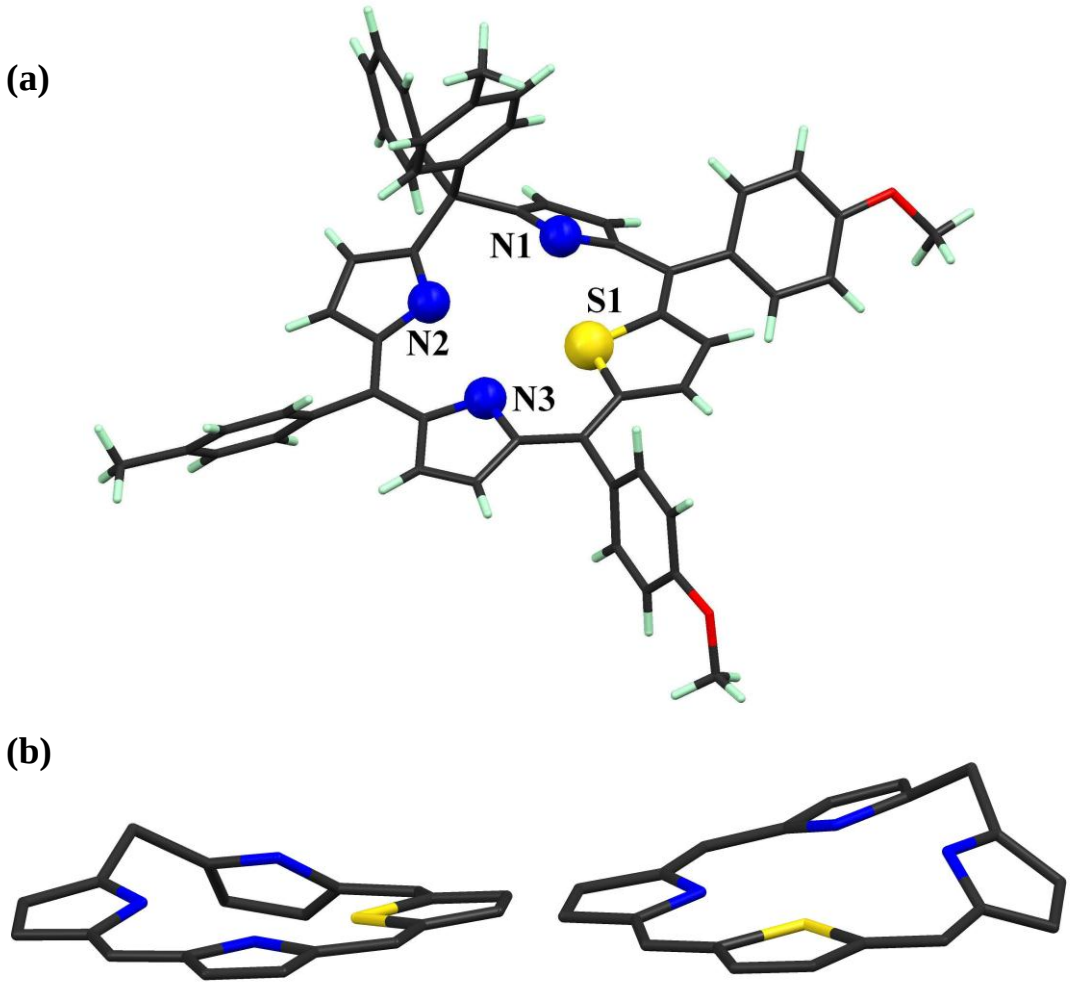


Figure S21. Single crystal X-ray structure of the compound **3**: (a) perspective view and (b) side view of compound **3** showing the distorted macrocyclic ring (*meso*-aryl rings and hydrogen atoms are omitted for clarity).

Table S2. Crystallographic data for compounds **2** and **3**.

Parameters	**2**	**3**
mol formula	$C_{54}H_{41}N_3S$	$C_{54}H_{41}N_3O_2S$
fw	763.96	795.96
cryst sym	Monoclinic	Monoclinic
Space group	P 21/n	P 21/c
a (Å)	11.1143(15)	10.921(3)
b (Å)	27.608(4)	17.486(5)
c (Å)	14.148(2)	22.220(6)
α (deg)	90.00	90.00
β (deg)	109.189(11)	102.828(13)
γ (deg)	90.00	90.00
V (Å^3)	4100.0(10)	4137(2)
Z	4	4
μ (mm^{-1})	0.121	0.126
D_{calcd} (g cm^{-3})	1.238	1.278
F(000)	1608	1672
2θ range (deg)	2.12 –25.03	1.50 – 25.03
Independent refections	7105 [R(int) = 0.1310]	7239 [R(int) = 0.1248]
R1, wR2 [$I > 2\sigma(I)$]	0.1029, 0.2265	0.0981, 0.2424
R1, wR2 (all data)	0.2380, 0.2911	0.2264, 0.3327
GOF	1.024	0.985
Largest diff. peak/hole, (e Å^{-3})	0.676, −0.601	0.420, −0.664

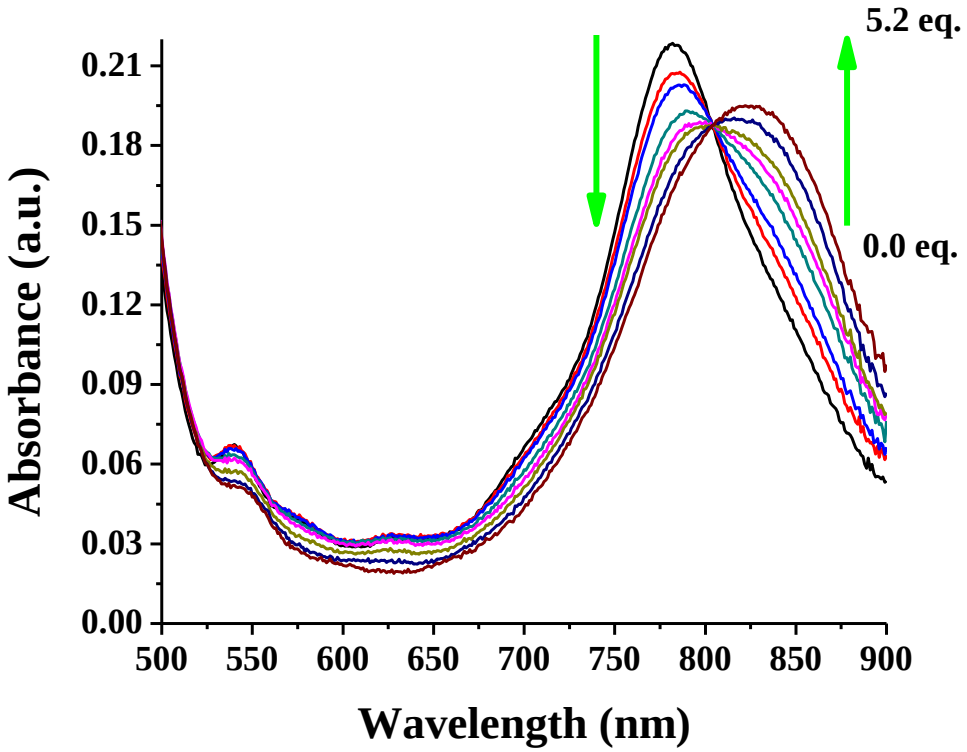


Figure S22. Change of absorption band during the anion binding study of the protonated form (in presence of TFA) of compound **2** (**2**·3H^{3+}) with F^{-} anion (tetrabutylammonium fluoride as F^{-} ion source) recorded in CH_2Cl_2 at room temperature. The concentration of the **2**·3H^{3+} was 10^{-5} M.

Experimental Section

Chemical. All general chemicals and solvents were procured from S.D. Fine Chemicals, India. Column chromatography was performed using silica gel and basic alumina obtained from Sisco Research Laboratories, India. Tetrabutylammonium perchlorate was purchased from Fluka and used without further purifications. All NMR solvents were used as received. Solvents like dichloromethane, tetrahydrofuran (THF) and *n*-hexane were purified and distilled by standard procedures.

Instrumentation. The ^{1}H and ^{13}C NMR (δ in ppm) spectra were recorded by using a Bruker AVANCE III 400 MHz spectrometer. Tetramethylsilane (TMS) was used as an internal reference for recording ^{1}H NMR spectra (residual proton; $\delta = 7.26$ ppm) in $CDCl_3$. The HR–MS spectra were recorded with a 'Bruker Maxis Impact' spectrometer. Absorption spectra were obtained with 'Cary 100 Bio' UV-visible spectrophotometer. The experiments were done in dry dichloromethane with 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte. Cyclicvoltammetry (CV) and differential pulse voltammetry (DPV) studies were carried out with a BAS electrochemical system by utilizing the three-electrode configuration consisting of glassy carbon (working electrode), platinum wire (auxiliary electrode), and saturated calomel (reference electrode) electrodes.

X-ray crystallography: Single crystal of suitable size for X-ray diffractometer were selected under a microscope and mounted on the tip of a glass fiber, which was positioned on a copper pin. The X-ray data for the compounds **2** and **3** were collected on a Bruker Kappa CCD diffractometer, employing graphite-monochromated Mo Kα radiation at 200 (2) K and the θ–2θ scan mode. The space group for the complex **2** was

determined on the basis of systematic absences and intensity statistics, and the structure of the compounds **2** and **3** were solved by direct methods using SIR92 or SIR97 and refined with SHELXL-97.[1] An empirical absorption correction by multi-scans was applied. All non-hydrogen atoms were refined with anisotropic displacement factors. Hydrogen atoms were placed in ideal positions and fixed with relative isotropic displacement parameters. CCDC 939918 and CCDC 939919 contain the supplementary crystallographic data of compounds **2** and **3** respectively for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General Synthesis. Free base porphyrin 5,10,15,20-tetra(*p*-tolyl)-21-thiaporphyrin **4** and 5,20-bis(*p*-methoxyphenyl)-10,15-bis(*p*-tolyl)porphyrin **5** were synthesized by following literature methods.[2]

General Synthesis of Compounds 2 and 3. 100 mg of the corresponding freebase porphyrin **4** or **5** in dry toluene (30 mL) was treated with 15 equivalent of $PhBCl_2$ under nitrogen atmosphere. The reaction mixture immediately turned into green colour and was slowly heated to reflux for 10 h. As the reaction progress, the colour of the reaction mixture turned into dark with greenish tint. The progress of the reaction was monitored by TLC analysis. After completion of the reaction, the excess $PhBCl_2$ was quenched by adding water to the reaction mixture. The reaction mixture was extracted with CH_2Cl_2 and the organic layers were collected, washed with water, dried over Na_2SO_4. The solvent was removed completely under reduced pressure. The crude solid was subjected to a basic-alumina column chromatography. The fast moving green band followed by

unreacted corresponding freebase porphyrin were collected separately with petrolim-ether/CH_2Cl_2 (7:3 and 3:2 respectively) solvent mixture. The dark green solid obtained from green fraction was subjected to a basic-alumina column chromatography for further purification. The fast green fraction afforded the corresponding compounds **1**/**2**. The compounds were recrystallized from CH_2Cl_2/*n*-hexane solvent mixture afforded shiny crystalline pure solids in good yields. When the reaction was performed in dry benzene the compounds **2** and **3** were also obtained in similar yield.

Compound 2. Yield 49 % (54 mg, 0.071 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (d, *J* (H,H) = 8.04 Hz, 2H, Ar), 7.47 (d, *J* (H,H) = 7.96 Hz, 2H, Ar), 7.39 (d, *J* (H,H) = 2.56 Hz, 1H, *β*-thiophene H), 7.37 (s, 2H, Ar), 7.27–7.24 (m, 9H, Ar), 7.20 (d, *J* (H,H) = 5.84 Hz, 1H, *β*-thiophene H), 7.05–6.99 (m, 4H, Ar), 6.92 (d, *J* (H,H) = 4.52 Hz, 1H, *β*-pyrrole H), 6.82 (d, *J* (H,H) = 8.20 Hz, 2H, Ar), 6.74 (d, *J* (H,H) = 4.16 Hz, 1H, *β*-pyrrole H), 6.67 (d, *J* (H,H) = 4.52 Hz, 1H, *β*-pyrrole H), 6.55 (d, *J* (H,H) = 3.72 Hz, 1H, *β*-pyrrole H), 6.19 (d, *J* (H,H) = 3.72 Hz, 1H, *β*-pyrrole H), 6.13 (d, *J* (H,H) = 4.16 Hz, 1H, *β*-pyrrole H), 2.46–2.44 (m, 9H, –CH_3), 2.31 (s, 3H, –CH_3). ^{13}C NMR ($CDCl_3$): δ = 144.93, 144.64, 141.47, 139.86, 138.45, 137.87, 137.39, 137.17, 137.15, 136.72, 136.55, 136.47, 135.57, 133.49, 132.58, 131.77, 131.72, 131.31, 129.85, 129.69, 129.30, 129.09, 129.01, 128.61, 127.95, 127.82, 127.48, 126.41, 125.53, 123.09, 120.42, 118.12, 114.68, 21.54, 21.48, 21.16 ppm. Uv-vis (λ_{max} nm (log ε), CH_2Cl_2): 340 (sh), 421 (4.61), 432 (sh), 625 (sh), 672 (4.19, br); **2+TFA**: 297 (sh), 395 (4.64), 470 (4.67), 539 (sh), 783 (4.45, br). HR–MS: m/z: 766.3265 $[M+2H]^+$. Anal. Calcd for $C_{54}H_{41}N_3S$: C, 84.89; H, 5.41; N, 5.50. Found: C, 84.24; H, 5.39; N, 5.48.

Compound 3. Yield 52% (57 mg, 0.072 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (d, *J* (H,H) = 8.72 Hz, 2H, Ar), 7.47 (d, *J* (H,H) = 7.96 Hz, 2H, Ar), 7.41 (d, *J* (H,H) = 8.64 Hz, 2H, Ar), 7.38 (d, *J* (H,H) = 5.84 Hz, 1H, *β*-thiophene H), 7.26–7.24 (m, 7H, Ar), 7.19 (d, *J* (H,H) = 5.84 Hz, 1H, *β*-thiophene H), 7.05–6.98 (m, 6H, Ar), 6.92 (d, *J* (H,H) = 4.52 Hz, 1H, *β*-pyrrole H), 6.83 (d, *J* (H,H) = 8.16 Hz, 2H, Ar), 6.73 (d, *J* (H,H) = 4.16 Hz, 1H, *β*-pyrrole H), 6.66 (d, *J* (H,H) = 4.52 Hz, 1H, *β*-pyrrole H), 6.55 (d, *J* (H,H) = 3.76 Hz, 1H, *β*-pyrrole H), 6.19 (d, *J* (H,H) = 3.72 Hz, 1H, *β*-pyrrole H), 6.13 (d, *J* (H,H) = 4.12 Hz, 1H, *β*-pyrrole H), 3.89 (s, 3H, $–OCH_3$), 3.88 (s, 3H, $–OCH_3$), 2.47 (s, 3H, $–CH_3$), 2.31 (s, 3H, $–CH_3$). ^{13}C NMR ($CDCl_3$): δ = 159.96, 159.01, 148.43, 144.99, 144.61, 141.44, 139.41, 137.82, 137.36, 137.11, 136.55, 135.98, 135.64, 135.02, 133.42, 133.05, 132.46, 132.42, 131.86, 131.76, 131.68, 129.80, 129.65, 128.96, 128.58, 127.93, 127.78, 127.46, 126.33, 125.49, 122.48, 120.45, 119.37, 118.13, 114.63, 113.77, 113.66, 55.49, 55.43, 21.50, 21.12 ppm. Uv-vis (λ_{max} nm (log ε), CH_2Cl_2): 339 (sh), 425 (4.57, br), 636 (sh), 675 (4.20, br); **3+TFA**: 296 (sh), 395 (4.54), 474 (4.60), 537 (sh), 645 (sh), 795 (4.42, br). HR–MS: m/z: 796.3003 $[M]^+$. Anal. Calcd for $C_{54}H_{41}N_3O_2S$: C, 81.48; H, 5.19; N, 5.28. Found: C, 81.02; H, 5.16; N, 5.23.

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